The single-stage sealing of ceramic tiles by means of high power diode laser radiation

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ABSTRACT

An investigation has been carried out using a 60 W high power diode laser (HPDL) to determine the feasibility of sealing the void between adjoining ceramic tiles with a specially developed grout material. A single-stage process has subsequently been devised using a new grout material which consists of two distinct components: a crushed ceramic tile mix substrate and a glazed enamel surface; the crushed ceramic tile mix provides a tough, inexpensive bulk substrate, whilst the enamel provides an impervious surface glaze. HPDL processing has resulted in crack and porosity free seals produced in normal atmospheric conditions. The single-stage grout is simple to formulate and easy to apply. Tiles were successfully sealed with power densities as low as 750 W/cm^2 and at rates of up to 420 mm/min. Bonding of the enamel to the crushed ceramic tile mix was identified as being primarily due to van der Waals forces and, on a very small scale, some of the crushed ceramic tile mix material dissolving into the glaze.

Key words: High power diode laser (HPDL); Ceramic tiles; Grout; Vitrify; Enamel; Glaze; Wettability; Bonding

I. INTRODUCTION

The ubiquitous glazed ceramic tile is currently applied in a multitude of places: from hospital operating theatres to industrial clean-rooms. Such a broad applications base is mainly due to the tiles' inherent versatility and outstanding mechanical, chemical and physical properties. Furthermore, ceramic tiles are considered to be one of the most cleanable surfaces available [1]. Ceramic tiles are typically applied to walls and floors using either tile grouts or adhesive, with tile grout (typically epoxy based) or silicon resin being used to fill the void between adjoining tiles. A major difficulty with tiled surfaces is that contaminants can enter into, and exit a space via a tiled surface, through the tile grouts used to fill the void between adjoining tiles, or in the case of silicon resin sealants, pass around the edges of the seal because the sealant is not fully adhered to the tile surface due the presence of small voids that increase in size over time along the sealant/tile interface [1]. The problem is compounded, owing to the tile grouts porosity, by water, germs and other harmful agents, which have the ability to permeate into cavities behind the tiles, corroding the bonding agent used to fix the tile to the substrate, the substrate itself or even the ceramic tile. Moreover, the predominant problem with commercially available tile grouts is that because they are very difficult to clean, over time they become contaminated, and have to be removed physically or mechanically.

Yet only an extremely limited number of studies have been carried out to address the problems attendant when using conventional tile grouts. Even fewer studies have been carried out to investigate the possibility of using lasers to provide a solution. Lawrence et al. [2-4] have exclusively pioneered the use of the high power diode laser (HPDL) to devise a two-stage ceramic tile grout sealing process. The process used a new grout material which comprises of two distinct components: an amalgamated oxide compound grout (AOCG) substrate and a glazed enamel surface. The HPDL was used firstly to treat the AOCG surface so that an amorphous enamel seal could be subsequently fired onto the AOCG. HPDL surface treatment was essential in order to modify the wettability characteristics of the AOCG such that the enamel frit would bond after HPDL firing. The HPDL two-stage ceramic tile grout sealing technique was shown to yield crack and porosity free seals. An examination of the mechanical, chemical and physical characteristics of the seals showed that the generation of the enamel surface glaze resulted in a seal with improved mechanical and chemical properties over those of conventional epoxy tile grouts.

In contrast, a number of workers have previously studied the sealing of engineering ceramic surfaces using lasers. The remelting of ZrO_2 based protective ceramic layers using a CO_2 laser [5] with power densities ranging from 8.5-17 kW/cm^2 was shown to markedly decrease the level of structural defects and the lamellar microstructure. Further, the CO_2 laser remelting of a number of oxide ceramic coatings has been found to effect significant improvements in corrosion resistance [6], whilst the CO_2 laser remelting of Al_2O_3 and Al_2O_3-TiO_2 coatings yielded and increase in hardness and wear resistance [7]. The remelting of ZrO_2 based protective ceramic layers plasma sprayed onto a variety of bond coats using continuous wave (CW) and pulsed CO_2 lasers [8, 9] revealed that a pulsed laser produced less cracks, whilst the use of external flowing gas, such as He or Ar, resulted in increased cracking. However, the laser treated surfaces in both studies displayed the phenomenon of delayed fracture due to unrelieved thermal stresses. The laser melting of plasma sprayed ceramic coatings based on Al_2O_3, TiO_2 and ZrO_2 by CW and pulsed CO_2 lasers [10] revealed that the extent of cracking was a function of the total energy input to the surface and the thermophysical properties of the ceramic coatings. Consequently it was concluded that to avoid cracking in such materials when remelting using the CO_2 laser, it was essential to pre-heat the workpieces to around 800^0C and thus reduce the thermal gradient [10]. Similarly, the CO_2 laser treatment of Al_2O_3 ZrO_2 and TiC [11-13] cladded layers on a variety of alloys has been shown to be a viable technique. What is more, Bourban et al. [14] found that the quality of CO_2 laser treated Al_2O_3-ZrO_2 cladded layers on mild steel was highly dependant on the thickness of the cladded layer itself. The surface modification ceramics with other industrial lasers besides the CO_2 laser has proved successful. After excimer laser treatment of the surface of Al_2O_3, Cappelli et al. [15] noted changes in the surface chemistry and morphology of the material, whilst Wu et al. [16] remarked on the fact that excimer laser treatment of Al_2O_3-SiC occasioned surface smoothing and an increase in the toughness of the material. The surface glazing of mullite with a HPDL by Schmidt and Li [17] resulted in a glaze that exhibited good adherence to the bulk ceramic but was severely cracked. Furthermore, the firing of vitreous enamel frits onto steel substrates using CW CO_2 laser irradiation has proved successful [18, 19]. The fired enamels were found to be well bonded to the substrate and displayed an undulating surface morphology with minor porosities and a uniform microstructure. In both studies, however, pre-heating in a furnace of the steel substrate to 200^0C was necessary in order to avoid microcracking. The firing of vitreous enamel frits onto

glass substrates using CO_2 lasers has also been studied. Using a 4 kW laser, conventional enamel frits containing PbO (to reduce the firing temperature) were fired onto flat glass sheets [20] and the resultant temperature development was analysed. Because of the localised heating nature of laser radiation, temperatures in excess of 1000^0C could be achieved without causing any deformation of the substrate glass. As such, it proved possible to fire PbO-free enamel frits [21]. What is more, the gloss and the smoothness of the laser fired enamel were comparable to those of conventional furnace fired enamels. However, in both studies, pre- and post-heating of the enamels in a furnace to temperatures in the range of the enamel melting temperature was necessary in order to relieve thermal stresses.

A new technique is presented in this paper whereby ceramic tiles are sealed together by means of a single-stage process using a HPDL without the need for pre-heating or special atmospheric conditions. The reasons behind the use of the HPDL, as opposed to other industrial lasers, are discussed at length elsewhere [2-4]. The seals generated between adjoining vitrified ceramic tiles described in the paper were found to be tough and inexpensive, as well as providing an amorphous, crack-free surface glaze. In this way the tiles were sealed together permanently, preventing any further contamination activity; in effect creating a completely sealed surface that is both impermeable and relatively simple to clean and maintain since contaminants are basically arrested on the surface of the tile and the glazed seal. Because such a seal would be an integral a part of the surface as the tiles themselves, the necessity to remove old or contaminated grout from the void between the tiles would be eliminated.

II. SINGLE-STAGE GROUT MATERIAL DEVELOPMENT

Commercially available epoxy tile grout is currently formulated from four main components: acrylic emulsion, limestone, dolomite and a cellulose substance. The limestone and dolomite act as fillers and the cellulose substance is added basically to thicken the grout. It is well established that glazing can only be achieved using materials containing at least some of the essential glass network forming compounds such as SiO_2 and BO_3, along with some glass network modifying and intermediate compounds such as Na_2O, Al_2O and MgO [22]. As such, it proved impossible to directly glaze epoxy tile grouts. Also, the coating of epoxy tile grout with a vitrifiable substance was not possible since the actual bonding mechanism by which

the grout adheres to surfaces to which it is applied is mechanical, or more precisely hydraulic, and is achieved as a result of the acrylic emulsion hydraulically bonding to the surface [23]. Since the grout does not bond to surfaces chemically, it is unable to withstand elevated temperatures. Indeed, at temperatures above 200^0C the grout will actually de-bond from the surface it is applied to [24], a temperature well below the softening point of commercial vitreous coating materials.

Based on the findings of previous work conducted by Lawrence et al. [2, 4], nine different oxide compounds and three types of enamel frit were chosen as the materials with which to develop the single-stage seal. The selected oxide compounds were obtained in powder form with various particle sizes. To ensure particle size consistency the powders were in turn fine ground with a pestle and mortar and then sieved through a 45 μm mesh. Details of the selected oxide compounds are given in Table 1. The enamel frits are commercially available and were obtained from Ferro Group (UK) Ltd. The compositions of the enamel frits consisted mainly of the following: SiO_2, B_2O_3, Na_2O, Mn, F and small quantities of Ba, Al_2O_3 and Ni, whilst the powder size was around 20 μm. The selected compounds and the selected enamel frits were then thoroughly mixed together in various compositions to ensure homogeneity, along with approximately 50% diluted sodium-silicate-solution so as to form a manageable paste. The single-stage grout mixtures in this paste form were then immediately applied to ordinary Portland cement (OPC) substrates (50 x 50 x 10 mm^3) and, according to the findings of cursory trials conducted to determine the optimum settling time, allowed to cure for 24 hours prior to the HPDL treatment. The thickness of the grout materials on the OPC substrate was monitored and kept at approximately 3 mm across the whole of the surface. Unfortunately it proved impossible to generate satisfactory glazes using any of these mixes; microcracking and porosity generation to varying degrees, as well as inconsistent glazing were ever present features (see Discussion). Consequently a new approach was adopted. Whereas previously the compounds and the enamel frit were combined together to form a single amalgamated mixture, the new approach specifically kept the compounds and the enamel frit apart. However, previous work by Lawrence et al.[2-4, 25, 26] revealed that in order for the enamel frit to wet and bond to the compound mixtures, HPDL surface treatment of the compound mixtures was necessary (so as to generate a vitrified surface) prior to the application of the enamel frit. The solution found for this problem was to use crushed

vitrified ceramic tiles as a bulk filler, since the enamel frit will readily wet this material without the need for prior HPDL surface treatment, with the enamel frit placed directly on top as shown in Fig. 1. In this way a single-stage process could be achieved as theoretically the materials could be applied in a single action and only one pass of the HPDL would be required.

III. LASER PROCESSING EXPERIMENTAL PROCEDURE

The experiments were carried out using UK standard 150 x 150 x 5 mm^3 vitrified ceramic tiles of various colours: white, navy blue, leaf green and jet black, cut into smaller pieces, 20 x 20 mm^2, for experimental purposes and applied in pairs to an OPC substrate using standard epoxy tile grout (Vallance Ltd). The spacing between the vitrified edges of each tile pair was the industry recommended 1.5 mm. The fixed ceramic tile pieces were then allowed to set for the standard setting time of one day. Vitrified ceramic tiles were crushed and fine ground using a pestle and mortar and then sieved to ensure a particle size of less than 45 μm. So as to form a manageable paste, the vitrified ceramic tile powder was mixed with approximately 50wt% water diluted sodium silicate solution. The vitrified ceramic tile paste was then placed into the void, flush to the surface of the tiles and allowed to cure for 8 h. The set mixture was then overlaid directly with a thin layer (500 μm) of enamel frit which, in order to form a manageable paste, was mixed with 20wt% white spirit. The enamel frit paste was allowed to cure for 1 h and then irradiated immediately with the defocused HPDL beam.

The laser used in the study was a surgical HPDL (Diomed Ltd.), emitting at 810 nm ±20 nm and operating in the CW mode with rated optical powers ranging from 0-60 W. The HPDL beam was delivered to the work area by means of a 4 m long, 600 μm core diameter optical fibre, the end of which was connected to a 2:1 focusing lens assembly mounted on the z-axis of a 3-axis CNC gantry table. The single-stage ceramic tile grout was irradiated using the defocused high order mode HPDL beam with a beam spot diameter of 1.75 mm and HPDL powers (measured at the workpiece after fibre and optics losses using a Power Wizard power meter) of 10-45 W. Fig. 2 illustrates the laser processing experimental arrangement, whereby the defocused HPDL beam was fired along the vitrifiable enamel frit placed in the void between adjoining vitrified ceramic tiles by traversing the samples beneath the HPDL beam using the x- and y-axis of the computerised numerical control (CNC) gantry table at speeds

ranging from 1-20 mm/s. In order to study the possible effects of different process gasses, 3 l/min of coaxially blown Ar or O_2 assist gas was used to shield the HPDL optics, whilst the fumes produced were removed with an extraction system. In order to analyse the HPDL treated specimens, they were sectioned with a Struers cutting machine using a diamond rimed cutting blade and then polished using cloths and diamond suspension pastes. The sectioned samples were then examined using optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) techniques.

IV. RESULTS

A. Operating window

The interaction between the enamel (frit) surface of the single-stage ceramic tile grout and the incident HPDL beam may be characterised by the irradiance and the interaction time (that is, if either one is independently altered then such a change can be compensated for through an independent alteration of the other). Accordingly, precisely structured and accurate experiments were conducted over a range of these variable to determine the exact operating window for the HPDL treatment of the single-stage ceramic tile grout (Fig. 3), within which good quality surface glazes displaying neither microcracks nor porosities could be generated.

B. General effects of laser radiation

1. Effect of laser power density on glaze morphology

Power density variations were observed to have a significant effect upon the surface morphology of the HPDL generated enamel glazes. A series of experiments were conducted with an O_2 shroud gas for a range of power densities and traverse speeds. A minimum power density level of around 1 kW/cm^2 was observed, below which incomplete glazing of the enamel occurred, regardless of the traverse speed. A typical example of a relatively low power density (1 kW/cm^2) HPDL glaze is the top track shown in Fig. 4. As one can see, HPDL interaction at this level resulted in a seal which appears only partially vitrified. At a relatively medium power density (2 kW/cm^2), however, the quality of the enamel surface glaze on the enamel was much improved. A typical example of a medium power density enamel surface glaze is the centre track shown in Fig. 4. Here complete vitrification of the

enamel has occurred, with the surface displaying no microcracks and no porosities. The bottom track shown in Fig. 4 shows an example characteristic of glazing within the relatively high power density range (3 kW/cm^2). As can be seen, the quality of the enamel surface glaze is extremely poor, displaying many large microcracks and porosities. Even so, both the microcracks and the porosities appear to be regular in both periodicity and intensity.

2. Effect of traverse speed on glaze morphology

As with power density variations, changes to the traverse speed had a significant effect upon the surface morphology of the enamel glaze. A series of experiments were conducted with an O_2 shroud gas for a wide range of traverse speeds and power densities. Typical results obtained at 2 kW/cm^2 for relatively low (<120 mm/min), medium (120-480 mm/min) and high (>480 mm/min) traverse speeds are shown in Fig. 5. From the experiments it was observed that typically, at relatively low and high traverse speeds, the surface condition of the enamel glazes were unacceptable. As the tracks on the top and bottom of Fig. 5 show, the glazed surfaces displayed many large porosities and microcracks. At traverse speeds in the range of 180-420 mm/min, however, good quality surface glazes on the enamel could be generated which displayed neither porosities nor microcracks (see Fig. 5, centre track).

3. Glazing/melting characteristics

Exposure of the crushed ceramic tile mix to rapid heating as a result of HPDL vitrification of the enamel frit results in further densification of the upper section of the crushed ceramic tile mix. This essentially entails the removal of the pores between the starting particles of the mix, combined with growth together and strong bonding between adjacent particles [27]. As the microscopic cross-sectional examination of the HPDL generated single-stage seal shown in Fig. 6 reveals, the crushed ceramic tile mix exhibits an upper densified layer, with a gradual decrease in the amount of densification as the depth increases. In addition, an XRD analysis of the crushed ceramic tile mix after HPDL vitrification of the enamel frit revealed that the structure was mainly polycrystalline in nature, with only partial vitrification taking place. This indicates that the densification of the upper sections of the crushed ceramic tile mix is achieved primarily by solid-state material transport, driven by differences in free-energy or chemical potential [27]. However, the fact that partial vitrification of upper section of the crushed ceramic tile mix was observed suggests that the formation of a liquid glass

phase was induced, which is often the case with ceramic materials [27]. Indeed, since the available reaction time is of the same order of magnitude as the interaction time, then it is probably too short to allow any significant solid-state diffusions to occur in this region. Hence reactions involving the liquid phase are more likely to contribute to interface adhesion.

C. The role of sodium-silicate-solution

As mentioned earlier, the crushed vitrified ceramic tile that acts as a bulk filler in the single-stage ceramic tile seal was mixed with approximately 50wt% water diluted sodium-silicate-solution so as to form a manageable paste. Sodium-silicate-solution is a viscous colourless solution of colloidal sodium silicate. It is a silica containing aqueous solution that, when combined with other solutions such as the crushed ceramic tile, forms a gel-like mass of silicate hydrate. Such a mass remains soft and malleable until it is exposed to CO_2 gas, either by means of a direct flow or through contact with the atmosphere, whereupon it hardens from the complete hydrolysis of the dissolved sodium silicate by the reaction [28]

$$Na_2SiO_3 + CO_2 \rightarrow Na_2CO_3 + SiO_2 \text{ (colloidal)} \qquad (1)$$

Notwithstanding this, exposure of the hardened mass to water results in a reversing of the process and the mass returns to a gel-like state. But, heating of the hardened mass fires the waterglass in effect (similar to that of a ceramic material) [28], increasing its strength and enabling it to withstand water exposure.

The thermal characteristics in relation to the compressive strength of the crushed ceramic tile bulk filler when mixed with the sodium-silicate-solution with increased temperature were investigated and are shown in Fig. 7. The strength of the crushed ceramic tile mix in terms of increasing temperature is determined primarily by the waterglass, since the strength of the individual oxide compounds which comprise the ceramic tiles vary little or not at all at relatively low temperatures ($<500^0$C) [29]. As is evident from Fig. 7, when the temperature is increased up to just beyond 125^0C the compressive strength of the crushed ceramic tile mix increases markedly from 6.2 MPa to a maximum of 22.7 MPa. This is due to the extensive dehydration of the silica gel between 100^0C and 150^0C, resulting in a gel mass which is water-free and therefore stronger [30]. Once the temperature exceeds 125^0C, however, the compressive strength of the crushed ceramic tile mix decreases sharply to 14.6 MPa where it remains almost consistently. The small interim increase in compressive strength observed at

around at 700^0C can be attributed to the crystallisation phenomena of the $Na_2O.2SiO_2$ within the waterglass [30]. The maximum compressive strength of 22.7 MPa for the crushed ceramic tile mix is considerably higher than that of commercially available waterproof ready mixed coloured tile grout, which has a maximum compressive strength of 10.5 MPa. Moreover, the general thermal resistance properties of the crushed ceramic tile mix were found to be far superior to those of the waterproof ready mixed coloured tile grout. Even at a temperature of 800^0C no breakdown of the crushed ceramic tile mix was observed, whereas waterproof ready mixed coloured tile grout is known to loose its integrity at temperatures above 200^0C [24]. Also, at temperatures above approximately 100^0C the complete irreversibility of the sodium-silicate-solution reaction, that is, the rehydration of the sodium-silicate-solution when exposed to water, was achieved.

As was shown earlier, without any exposure to heat the crushed ceramic tile mix will harden simply through contact with the atmosphere according to (1). Even so, the fact that the crushed ceramic tile mix in this state is hydraulically bonded, as opposed to chemically bonded, combined with the retention of chemical and mechanical water (that is water that is bonded into the materials matrix and water that is added respectively) means that the hardened mass will rehydrate when exposed to water [28, 30]. Heating of the crushed ceramic tile mix in this state is similar in effect to the firing of ceramic, in that the heating causes gradual ceramic sintering of the materials; dehydrating the mechanical water, dehydroxylating the chemical water and generally bonding together and stabilising the substances, until at around 100^0C sufficient pyrochemical changes have occurred to prevent any rehydration of the crushed ceramic tile mix [28, 31].

D. Bonding characteristics

The typical bond region between the enamel glaze and the crushed ceramic tile is shown in Fig. 8. As Fig. 8 shows, there is no dendritic growth in the bond region which is characteristic of enamels fired onto substrates containing Fe, Si and, in particular, Co [32]. However, as one can see from Fig. 8, small, but nonetheless discernible microstructural changes at the interface between the crushed ceramic tile mix and the enamel are apparent. Moreover, an EDX analysis carried out across the cross-section of the seal (within the enamel

glaze, the crushed ceramic tile mix and the interface region) revealed the presence of an area in which elements unique to both the enamel frit and the crushed ceramic tile mix existed.

V. DISCUSSION

The failure to generate complete glazes with the single-stage tile grout combinations detailed previously in Section II along the full length and breadth of the HPDL interaction zone can be attributed almost entirely to the wettability and bonding characteristics of the molten optimum single-stage tile grout. The bonding of particles takes place by means of localised laser induced heating, shown schematically in Fig. 9. The duration of the laser beam incident on any one particle is short, typically between 1.75 s and 0.88 ms. Consequently, the thermally-induced bonding reactions must be kinetically rapid. Two such mechanisms are viscous flow when the powder has the appropriate temperature dependant viscosity and melting.

Viscous flow has been described by Frenkel [33] using a two-sphere model. For the early stages of particle bonding, the neck of radius y joining two spheres of radius a grows according to:

$$\frac{y^2}{a} = \frac{2}{3}\left(\frac{\gamma}{\mu}\right)t \qquad (2)$$

where γ is the particle surface energy and μ is the thermally activated particle viscosity. Similar relations have been developed for spheres considering various atomic rearrangement mechanisms to accommodate densification [34]. While the exact form varies considerably depending on the mechanism being considered, the neck growth rate is always directly proportional to γ and thermally activated. The laser induced densification (due to melting and/or vitrification) rate in the early stages of laser densification, or sintering, often reveals an inverse viscosity dependence [34-36]. Sun et al. [37] have derived a sintering rate equation based on Frenkel's assumptions and the 'shrinking cube' geometry depicted in Fig. 10. The sintering rate, x_r, is given by

$$x_r = -\frac{3(1-\rho)\pi\gamma a^2}{24\mu\rho^3 x^3}\left\{r-(1-\xi)x+\left[x-(\xi+\frac{1}{3})r\right]\frac{9(x^2-r^2)}{18rx-12r^2}\right\} \qquad (3)$$

where $2x$ is the cube side dimension defined from Figure 5.4, r is the sphere radius and ρ is the apparent density. The variable ξ, ranging between 0 and 1, represents the probability of forming a neck between two arbitrary particles. From a statistical thermodynamics viewpoint, it is related to the energy status of the contact region. The reciprocal viscosity dependence of sintering rate is still maintained.

Materials with strongly temperature-dependent viscosities (or low activation energy for viscous flow) have been readily processed using laser radiation. Such materials include a number of thermoplastic polymers and rubber. Even at temperatures approaching the melting point, metals and ceramics are orders of magnitude more viscous than polymeric materials. For this reason, solid-state bonding mechanisms are not applicable for laser sintering. Thus a melting/solidification approach has been developed [38]. Attempts to laser sinter a number metals [39, 40] and ceramic materials [2, 4, 26, 27] have revealed the phenomena of 'balling'. Here, when melting has been induced by the laser beam, the molten powder consolidates rapidly into a spheres approximately equal to the laser beam diameter rather than consolidating into a continuous layer. Such an occurrence was observed after HPDL interaction with the initial single-stage tile grout mixtures. It is believed that balling of the initial single-stage tile grout compounds was caused by the material possessing a low melt viscosity which in turn allows surface energy effects to determine the final geometry. As such, since the molten material is often completely contained by loose powder rather than a fully dense material, then this powder is unable to exert tensile traction on the liquid to confine the melt to a layerwise geometry.

As mentioned previously, within the optimum operating parameters, the HPDL fired enamel glazes on the surface of the single-stage tile grout seals generally displayed neither porosities nor microcracks. The major reason for this highly beneficial occurrence is the value of the thermal gradient, ΔT, induced in the enamel during HPDL irradiation. This is due partly to the fact that the softening point of the enamel powder is around 500^0C, thus the tensile stresses that result from the unrelieved elastic stresses that occur due to the contraction of the material between the softening point (500^0C) and ambient temperature (20^0C) are reduced to a value well below that of the fracture strength of the enamel. The thermal stress, σ, induced by a thermal gradient can be calculated using the Kingery equation:

$$\sigma = \frac{E\alpha\Delta T}{1-\upsilon} \tag{4}$$

where, E is Young's modulus, α is the coefficient of thermal expansion and ν is Poisson's ratio. ΔT is the difference between the critical temperature (below which stresses can no longer be relieved) and ambient temperature. For the enamel used this is the difference between the softening point, 500^0C and ambient temperature 20^0C. Since the softening point of the enamel is 500^0C, that is the enamel can be plastically deformed at temperatures above 500^0C, then the thermal stresses arising during cooling from above 500^0C are relieved by plastic deformation. But unrelieved elastic stresses result due to contraction occurring between 500^0C and ambient temperature. Thus for the enamel used $\Delta T=480^0$C. So, by using the following values for the enamel: $E=6.25 \times 10^4$ MN/m^2, $\alpha=33 \times 10^{-7}$ K^{-1} and $\nu=0.162$ [41] and introducing them into Eq. (4), the thermal stress induced in the enamel during HPDL irradiation is calculated to be 118 MN/m^2. This value is below that of the fracture strength of the enamel, 135 MN/m^2 [41], and as such cracking will not occur, thus rendering any pre- or post-heating of the enamel completely unnecessary.

According to the types of materials used, complex combinations of the various bonding mechanisms actually come into play [42]. For the crushed ceramic tile mix and the enamel, the mechanisms involved in ceramic-glass bonding are reasonably applicable. These principally include: physical bonding (van der Waals forces), chemical bonding (oxide transformation and O_2 bridging) and on a very small scale, electrochemical reactions such as the electrolytic effect (redox reaction) due to the presence of ferric oxides within the crushed ceramic tile mix reacting with other oxides in the enamel [42]. However, in the case of the crushed ceramic tile mix and the enamel, the predominant bonding mechanism results from physical forces; since adhesion between many materials is assured by electron transfer and is thus related to bandgap energy [43]. Thus for non-conducting materials, such as the crushed ceramic tile mix, with large bandgaps, there will be practically no free charges inside the ceramic crystals, even at elevated temperatures. In this case the electron transfer at the interface will not take place since the electron transfer depends exclusively on the concentration of free charges in the ceramic crystal [43]. As a result, the chemical contribution to the work of adhesion is negligible [43]. Notwithstanding this, the bonding mechanism between the HPDL treated crushed ceramic tile mix and the enamel is not entirely

due to physical forces. As Fig. 8 shows, slight microstructural changes at the interface between the crushed ceramic tile mix and the enamel are evident. Indeed, it is well known that Na^+ is extremely mobile and can, therefore, diffuse to create an interfacial zone of intermediate composition. Furthermore, DeHosson *et al.* [44, 45] have observed that chemical reactions between individual phases can occur during the laser processing of multiphase ceramics. But such an interfacial zone was not observed during a cross-sectional EDX analysis of the bond region. However, an EDX analysis conducted across the cross-section of the seal did reveal an area which contained elements unique to both the enamel frit and the crushed ceramic tile mix. Such a finding is in accord with those of Greenhut [42] who established that enamel glazes on ceramic materials such as the crushed ceramic tile mix are typically bonded as a result of some of the base material dissolving into the glaze.

VI. CONCLUSIONS

Ordinary vitrified ceramic tiles have been successfully sealed using a 60 W high power diode laser (HPDL) with power densities as low as 750 W/cm^2 and at rates as high as 420 mm/min. A single-stage process has been devised using a crushed ceramic tile mix and a commercially available vitreous enamel. The crushed ceramic tile mix provides a tough, inexpensive bulk substrate which simply acts a filler for the void between adjoining tiles, whilst the enamel provides an impervious surface glaze. The thermal characteristics of the single-stage ceramic tile seal proved to be far superior to those of conventional epoxy tile grout, with complete integrity of the single-stage seals being observed at temperatures as high as 500^0C, whereas the conventional epoxy tile grout was found to fail completely at temperatures in excess of 200^0C.

It is believed that the failure to generate complete glazes with the initial single-stage ceramic tile grout compounds or an amalgamation of the crushed ceramic tile mix and the enamel frit, regardless of the ratios used, can be attributed to the wettability and bonding characteristics of the materials. More specifically, because the molten material is often completely contained by loose powder rather than a fully dense material, then this powder is unable to exert tensile traction on the liquid to confine the melt to a layerwise geometry. Hence attempts to seal these initial single-stage grout mixtures with the HPDL resulted in the formation of solid

spheres approximately equal in diameter to the width of the HPDL beam, a phenomena known more commonly as 'balling'.

Bonding of the enamel to the crushed ceramic tile mix was identified as being mainly due to van der Waals forces (dispersion forces) and, on a very small scale, slight microstructural changes occurring at the interface between the crushed ceramic tile mix and the molten enamel resulting in some of the crushed ceramic tile mix material dissolving into the glaze.

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List of Figs.

FIG. 1

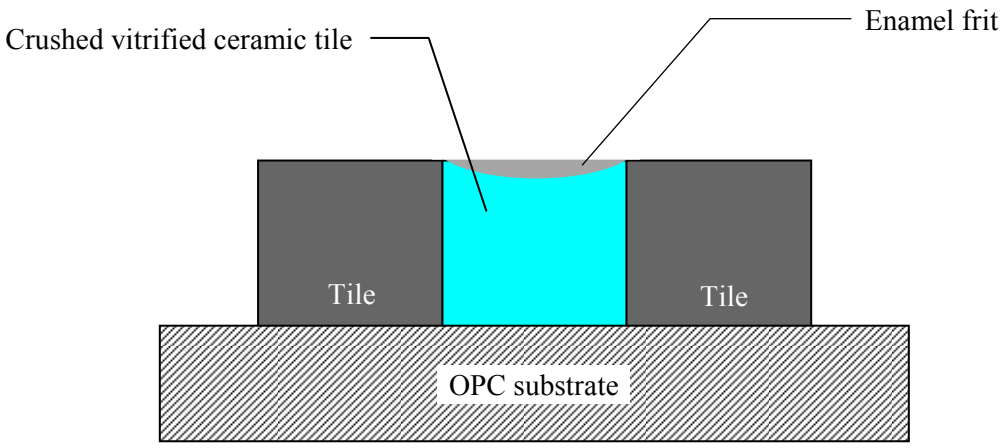

Crushed vitrified ceramic tile
Enamel frit
Tile
Tile
OPC substrate

FIG. 2

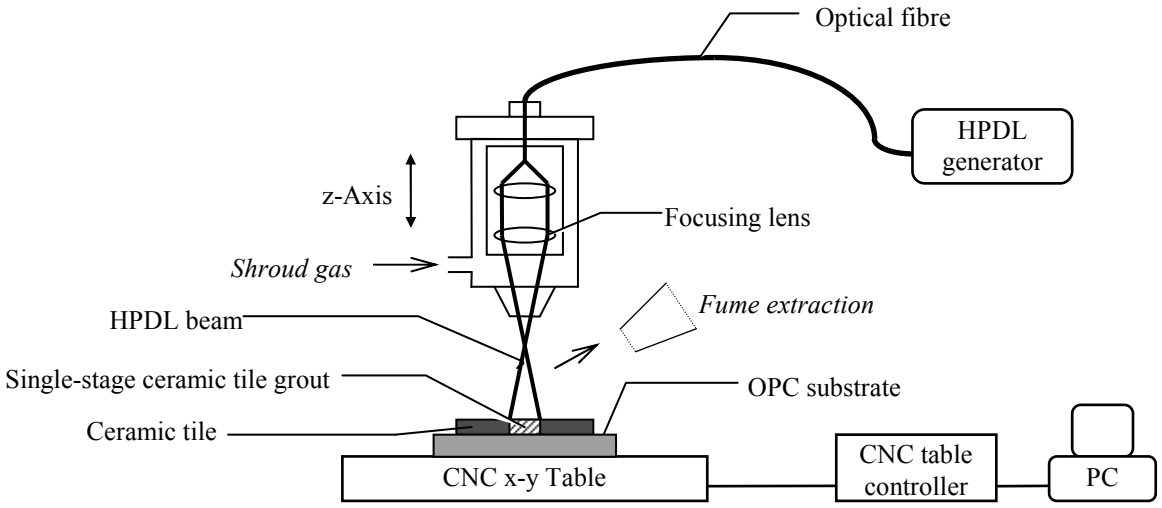

Optical fibre
HPDL generator
z-Axis
Focusing lens
Shroud gas
Fume extraction
HPDL beam
Single-stage ceramic tile grout
OPC substrate
Ceramic tile
CNC x-y Table
CNC table controller
PC

FIG. 3

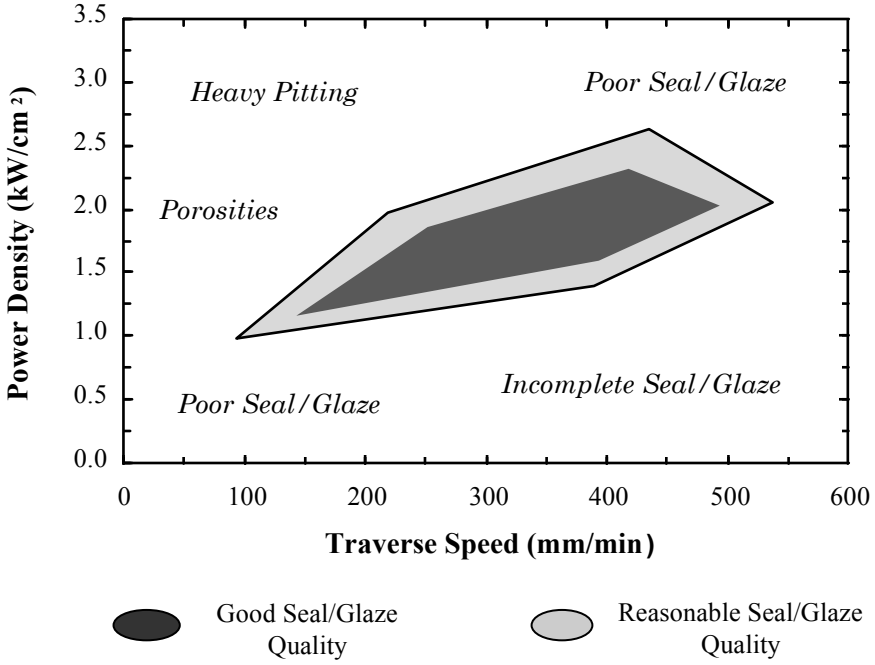

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Power Density (kW/cm²)
Heavy Pitting
Poor Seal/Glaze
Porosities
Incomplete Seal/Glaze
Poor Seal/Glaze
0
100
200
300
400
500
600
Traverse Speed (mm/min)
Good Seal/Glaze Quality
Reasonable Seal/Glaze Quality

FIG. 4

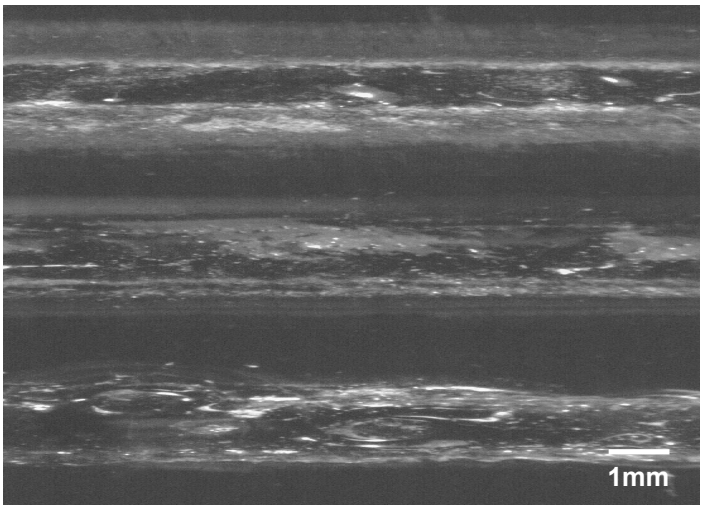


FIG. 5

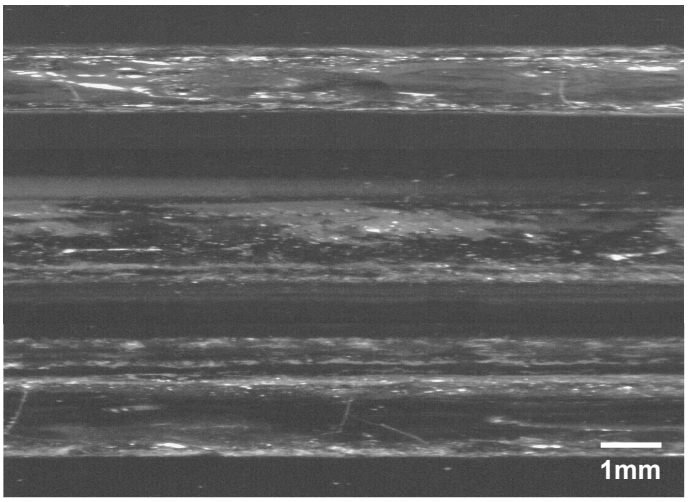


FIG. 6

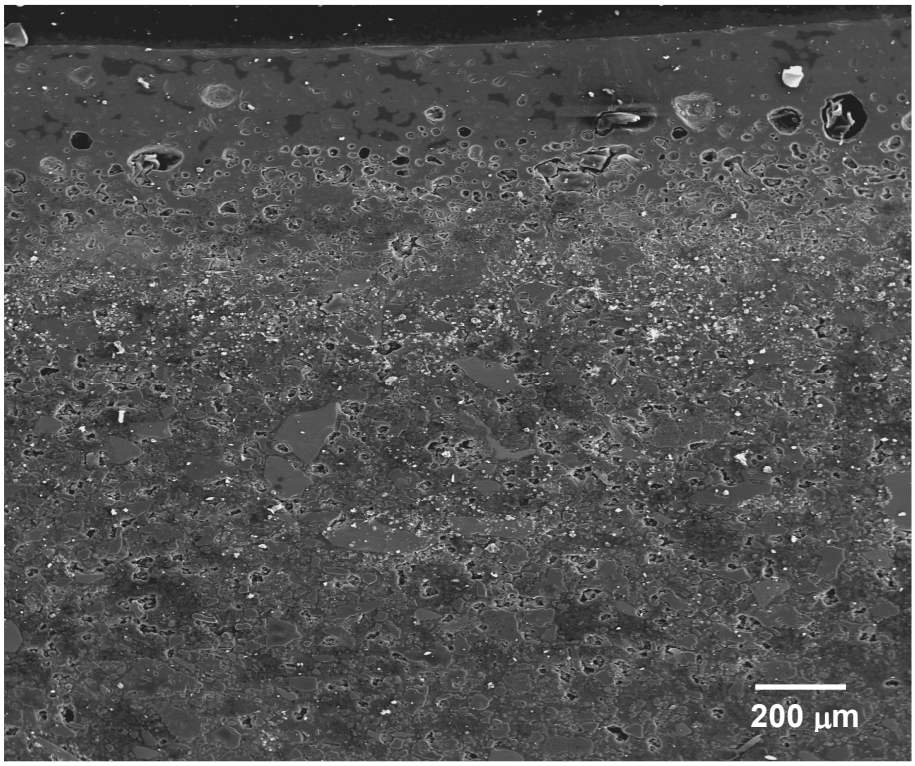


FIG. 7

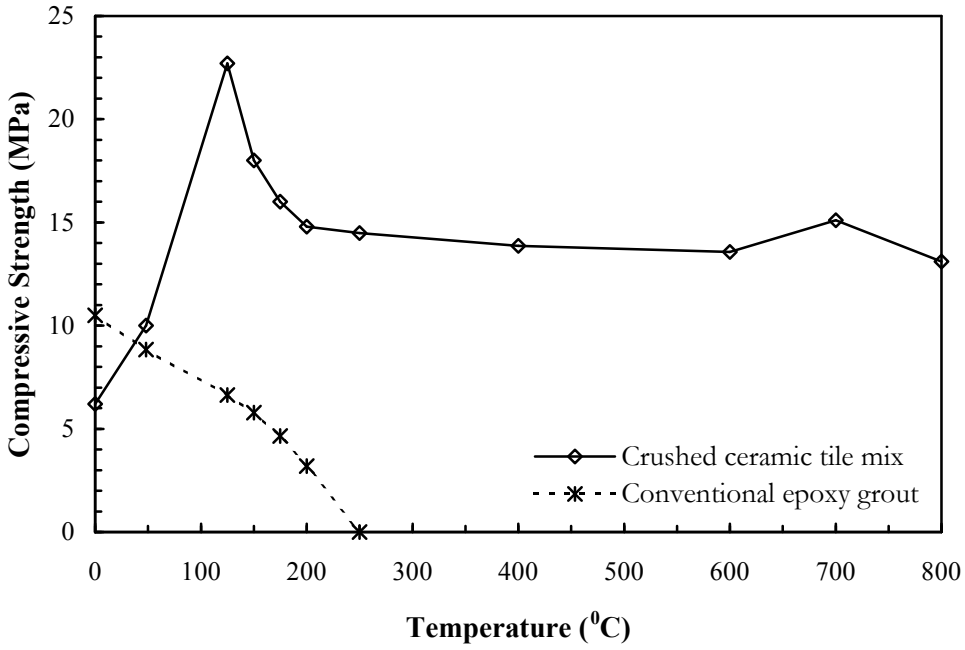

Compressive Strength (MPa)
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
Temperature (^{0}C)
Crushed ceramic tile mix
Conventional epoxy grout

FIG. 8

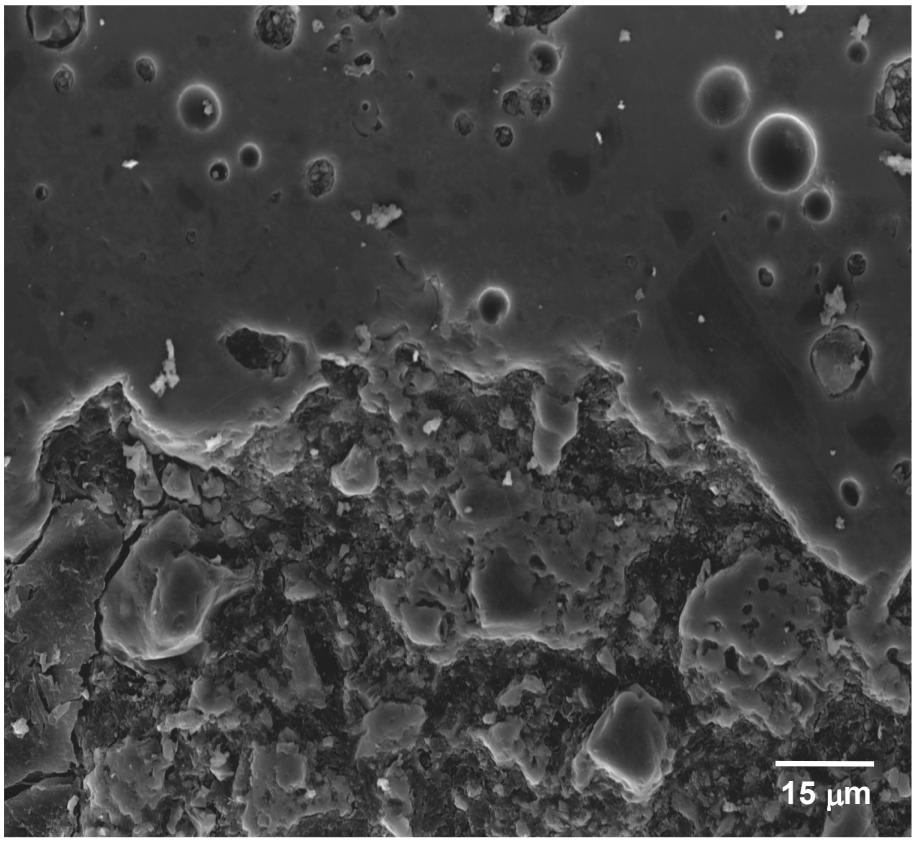


FIG. 9

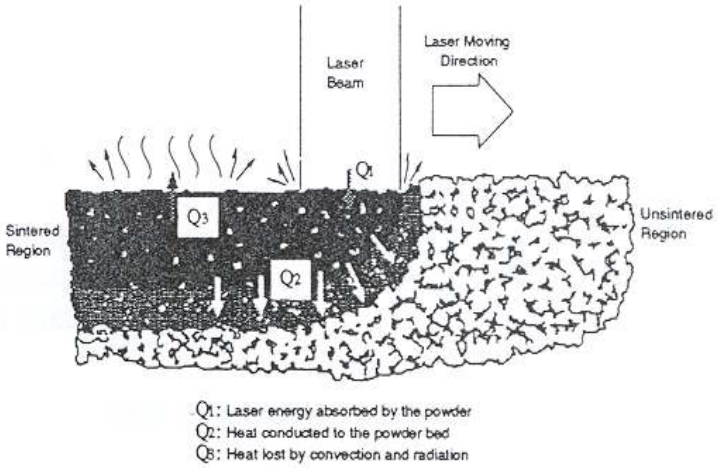
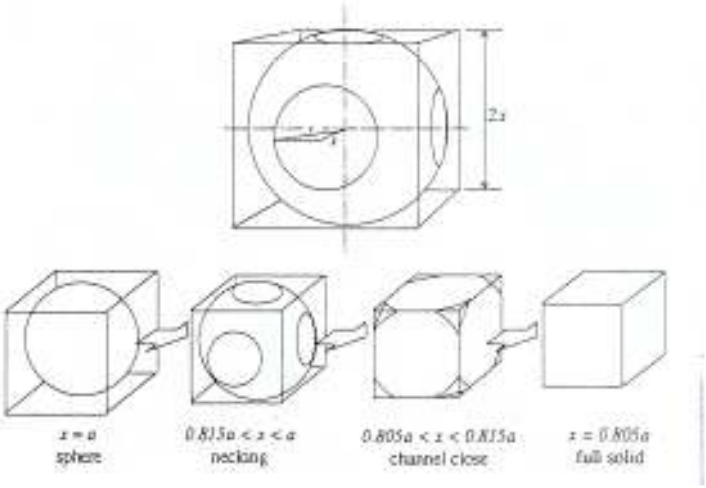

Laser Moving Direction
Laser Beam
Q1
Q3
Q2
Sintered Region
Unsintered Region
Q1: Laser energy absorbed by the powder
Q2: Heat conducted to the powder bed
Q3: Heat lost by convection and radiation

FIG. 10


2z
z = a
sphere
0.815a < z < a
necking
0.805a < z < 0.815a
channel close
z = 0.805a
full solid

List of Tables

Table 1

Material	Characteristics imparted when vitrified
Pozzolana	Volcanic dust comprised mainly of Al_2O_3 and SiO_2. Acts as a filler material in the compounds. After laser irradiation produces a hard, brittle dark coloured surface glaze.
Chamotte	Consists mainly of Al_2O_3, TiO_2 and SiO_2. Acts as a filler material in the compounds. After laser irradiation results in a glaze with very few cracks or porosities being visible.
Al_2O_3	Glass network intermediate compound. Increases the viscosity and lends toughness. Improves the stability towards devitrification and durability.
SiO_2	Glass network former. Increases the thermal strength by reducing the thermal expansion coefficient. Increases the resistance to thermal shock as well as increasing the softening temperature and viscosity.
Fe_2O_3	Reduces the amount of oxygen released during reaction and therefore reduces the surface blistering and small porosities.
FeS_2	Reduces the amount of oxygen released during reaction and therefore reduces the surface blistering and small porosities.
Zn	Imparts fluidity (reduces the viscosity) and ease of melting without affecting the thermal expansion. Also increases the resistance to thermal shock.
MgO	Glass network modifier. Lowers the softening temperature. Reduces the number of network bonds and therefore reduces the viscosity. Has a beneficial stabilising effect.
ZrO_2	Improves the chemical durability and resistance to thermal shock.